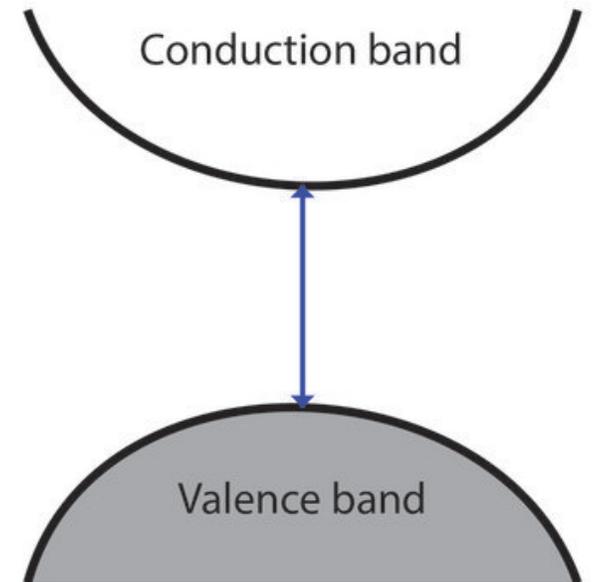


# What is a bandgap and how to compute it ?

Antton Curutchet

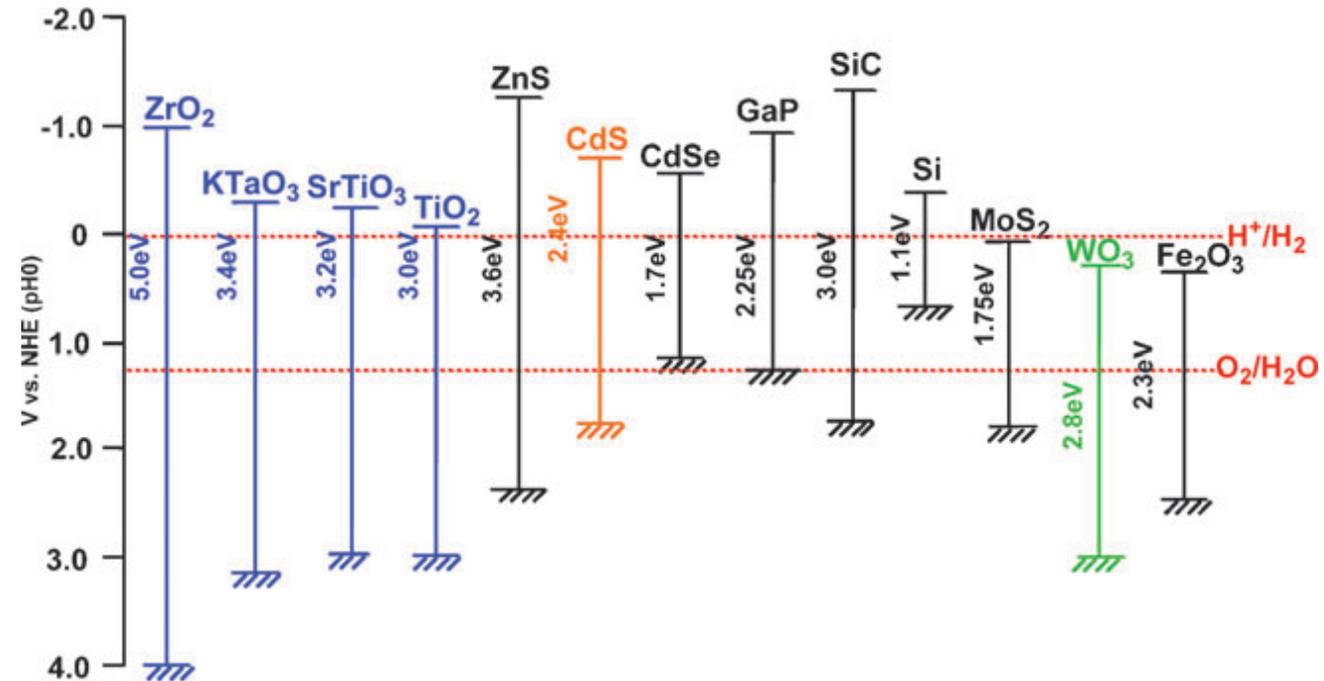
Group meeting

27th April



# Introduction

Concept of Gap in the heart of Photochemistry, Semiconductor sciences, ...



→ Many definitions of the « energy gap », that may differ

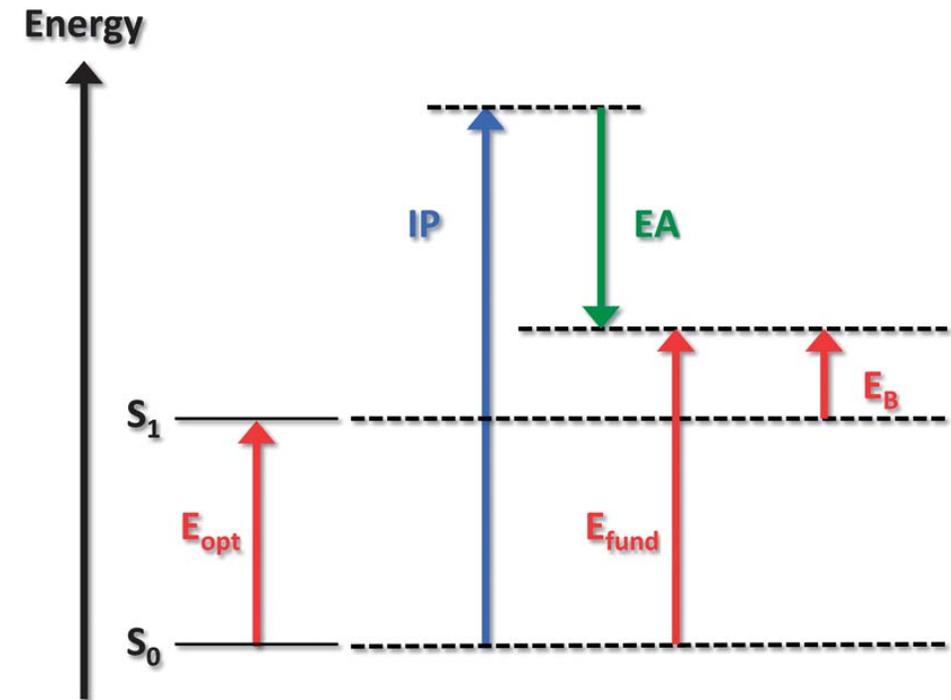
# Overview

1. Different approaches to the concept of bandgap
2. Computing bandgap with DFT
3. Why hybrid functionals ?

# 1. Different definitions around the concept of bandgap

## a) For an organic chemist

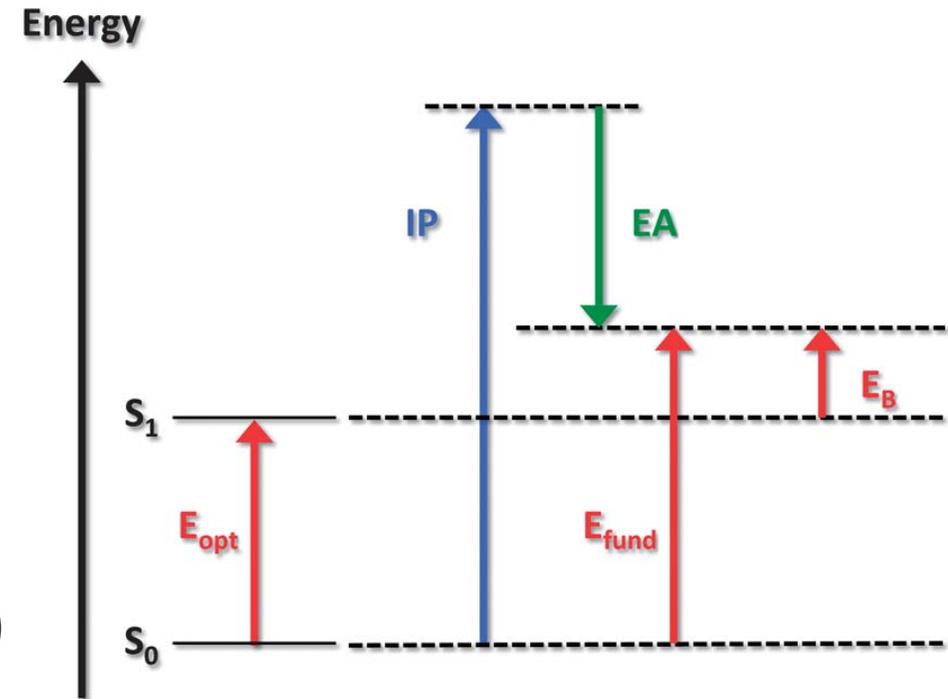
- HOMO-LUMO gap:  $E(\text{LUMO}) - E(\text{HOMO})$   
Calculated value
- Fundamental gap:  $\text{IP} - \text{EA} = E(N-1) - E(N) - [E(N) - E(N+1)]$
- Optical gap: Lowest 1-photon transition energy  
 $\rightarrow = E_{\text{fund}} - E_{\text{B}}$  (binding energy)
- Koopman's theorem:  $E(\text{HOMO}) = -\text{IP}$  and  $E(\text{LUMO}) = -\text{EA}$ , approximation



# 1. Different definitions around the concept of bandgap

## b) For a solid-state chemists

- band gap:  $IP - EA$   
(= fundamental gap)
- Optical gap:  $E_{\text{band gap}} - E_B$  (binding energy)  
→  $E_B$  smaller than for molecules ( $\sim \text{meV}$ )
- Bandgap measured by : XPS, optical absorption, photoluminescence

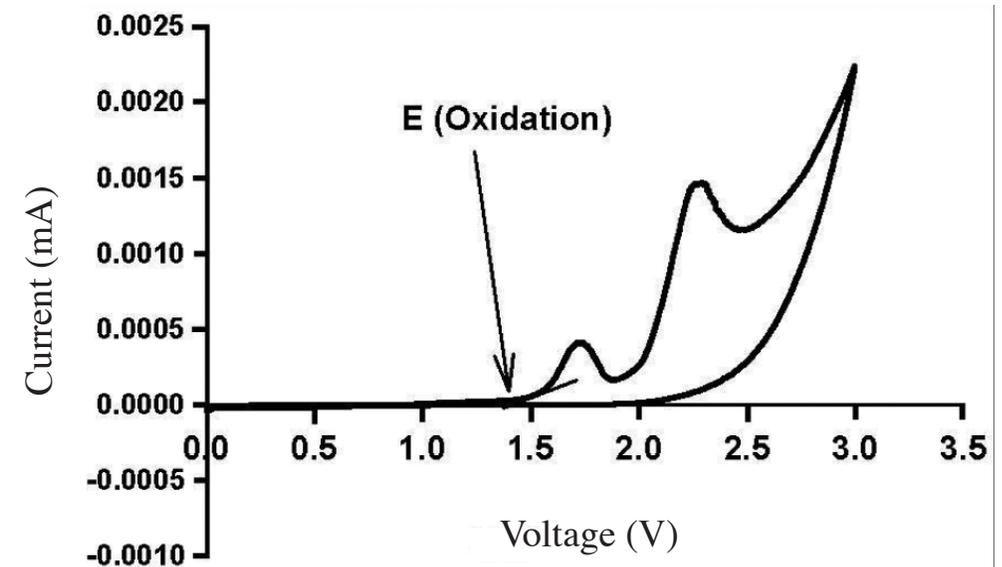


# 1. Different definitions around the concept of bandgap

## c) For an electrochemist

- Band gap = Energy derived from Oxidative / Reductive potentials obtained by CV

→ Solvent effects (surface polarisation)



# 1. Different definitions around the concept of bandgap

## d) For a theoretical chemist

- Band gap:  $g = \epsilon_{\text{BOCB}} - \epsilon_{\text{TOVB}}$  monoelectronic

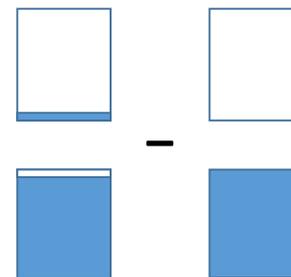
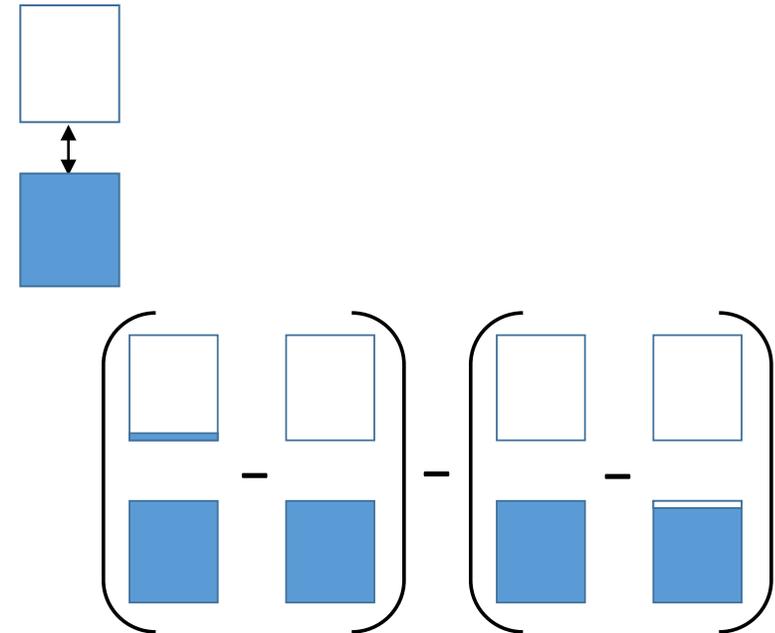
- Fundamental gap:

$$G = IP - EA = E(N-1) - E(N) - [E(N) - E(N+1)]$$

$$= E(N+1) - E(N) - [E(N) - E(N-1)]$$

→ Ground state energy difference

- Optical gap → need to compute excited states



## 2. Computing bandgap with DFT

### a) Computing $g$ and $G$

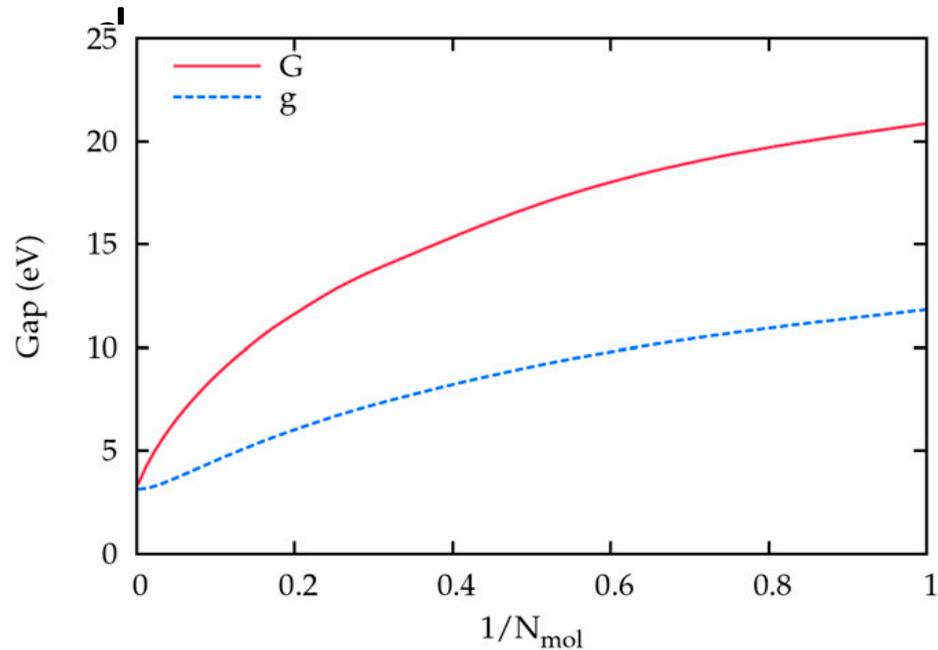
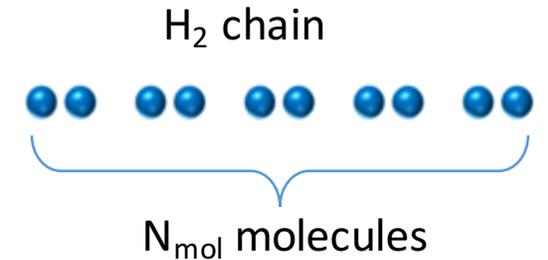
Kohn Sham method  $\rightarrow$  Description of ground state energy from a non-interacting system, through the choice of accurate XC functional  $E_{xc}[\rho]$

$$E[\rho] = T_S[\rho] + \int dr \cdot v_{ext}(r)\rho(r) + E_H[\rho] + E_{XC}[\rho]$$

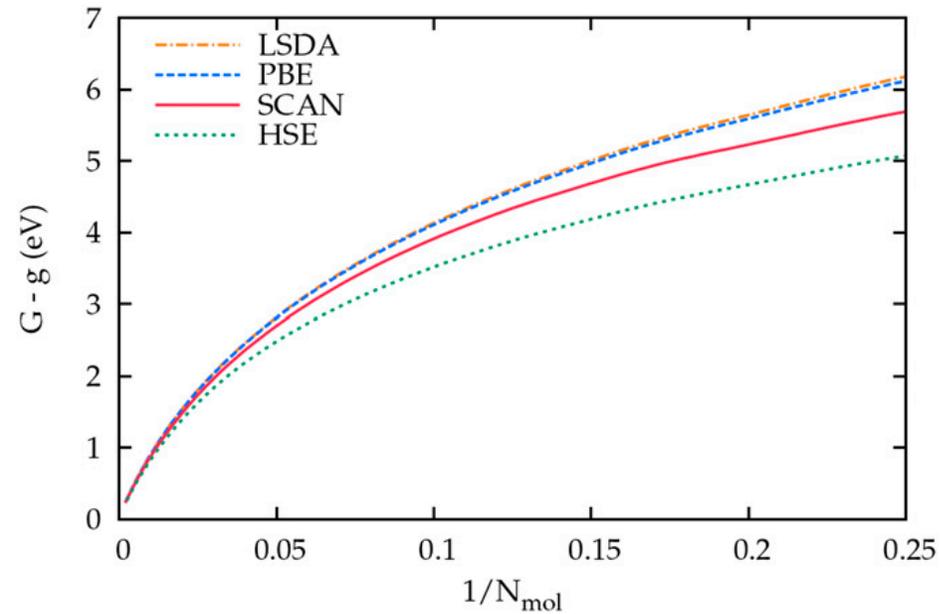
- Total energy : accurate  $\rightarrow$  linked to  $G$
  - Orbitals : Hypothetical  $\rightarrow$  linked to  $g$
- $\rightarrow$   $g$  has no reason to be accurate as KS eigenvalues are monoelectronic and should not have physical meaning.
- $\rightarrow$  Adding / removing electrons to extended systems is complicated

## 2. Computing bandgap with DFT

### b) Is $g$ equal to $G$ ? Numerical demonstration



**Fig. 1.** PBE GGA fundamental gap  $G$  and band gap  $g$  for a linear chain of  $N_{mol}$  H<sub>2</sub> molecules. Note that  $G$  converges to the limit  $N_{mol} \rightarrow \infty$  much more slowly than  $g$  does.



**Fig. 2.** Difference between the fundamental gap  $G = I - A$  and the GKS band gap  $g = \epsilon^{LU} - \epsilon^{HO}$  for a linear chain of  $N_{mol}$  hydrogen molecule.

→ Within numerical accuracy, as  $N \rightarrow \infty$ ,  $I \rightarrow -\epsilon^{HO}$ ,  $A \rightarrow -\epsilon^{LU}$ , and  $G \rightarrow g$

## 2. Computing bandgap with DFT

### **b) Is $g$ equal to $G$ ? Theoretical understanding**

Let's add and remove 1 electron to the fundamental state :

- Janak's theorem : 
$$\frac{\partial E}{\partial n_i} = \epsilon_i$$

## 2. Computing bandgap with DFT

### b) Is $g$ equal to $G$ ? Theoretical understanding

Let's add and remove 1 electron to the fundamental state :

- Janak's theorem:  $\frac{\partial E}{\partial n_i} = \varepsilon_i$

The density change is very small and delocalized  $\Rightarrow E$  is linear in  $n_i$

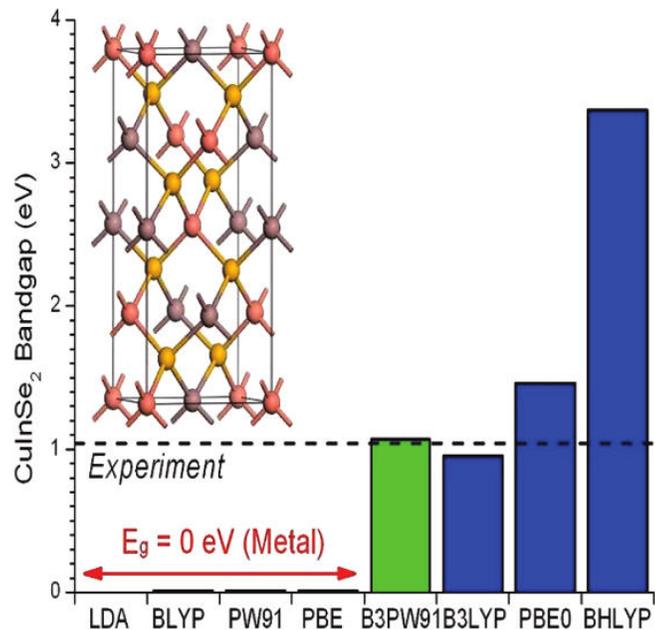
$$\Delta E^- = E(N) - E(N - 1) = \varepsilon_{HO} \cdot \Delta N = \varepsilon_{HO}$$

$$\Delta E^+ = E(N + 1) - E(N) = \varepsilon_{LU} \cdot \Delta N = \varepsilon_{LU}$$

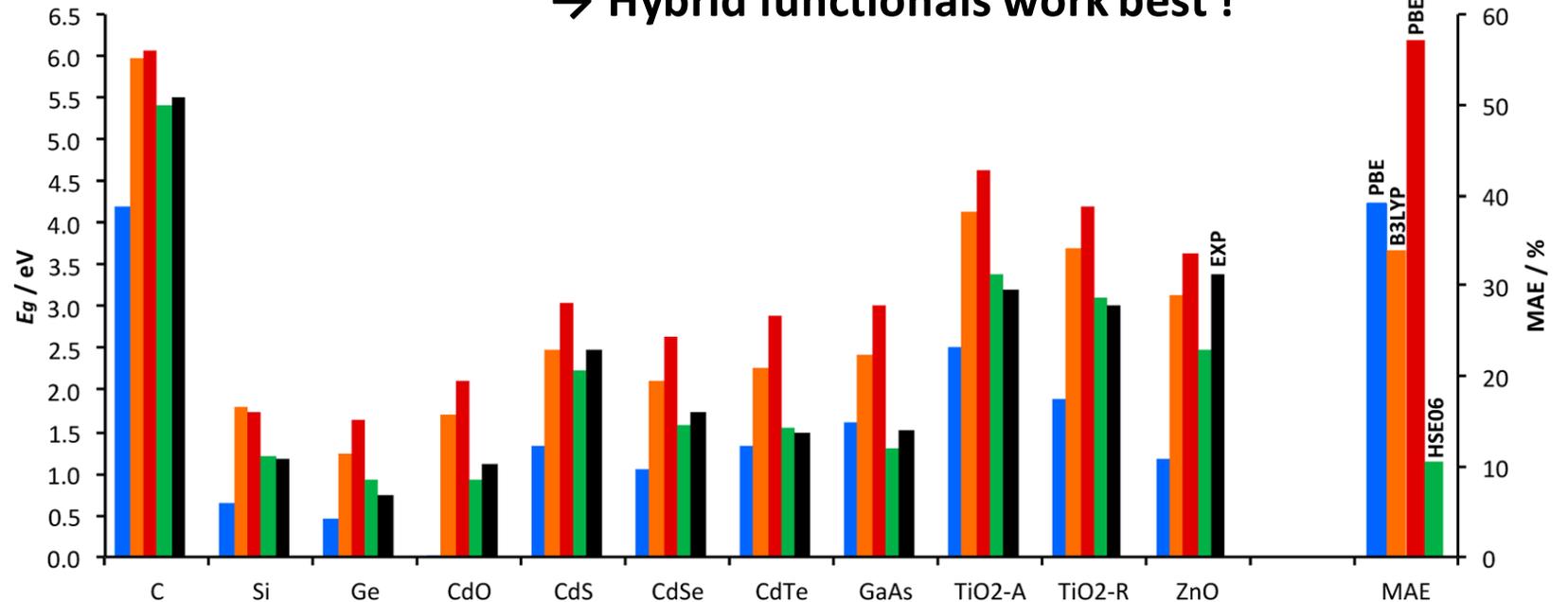
Therefore  $g = \varepsilon_{LU} - \varepsilon_{HO} = IP - EA = G$

# 3. Why hybrid functionals ?

## a) Bandgaps and functionals



→ Hybrid functionals work best !



Computed gaps (in eV) along with the MAE (in %). The colors blue, orange, red, green, and black correspond to PBE, B3LYP, PBE0, HSE06, and experiment, respectively.

### 3. Why hybrid functionals ?

#### **b) Comparison of hybrid and non-hybrid functionals**

- LDA, GGA functionals are spatially local, while HF exchange functional is non-local
- When an electron is added or removed, the density change should be infinitesimal and periodic

### 3. Why hybrid functionals ?

#### c) Choice of HF amount

Too low %HF : Underestimation of bandgap

Too high %HF : Overestimation of bandgap

Best results for %HF =  $\frac{100}{\epsilon_{\infty}}$  → Best functional depends on the semiconductor

Thank you for your attention !